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**PAPER**

# Highly-controlled regiospecific free-radical copolymerization of 1,3-diene monomers with sulfur dioxide†

**Naruki Tanaka, Eriko Sato and Akikazu Matsumoto***

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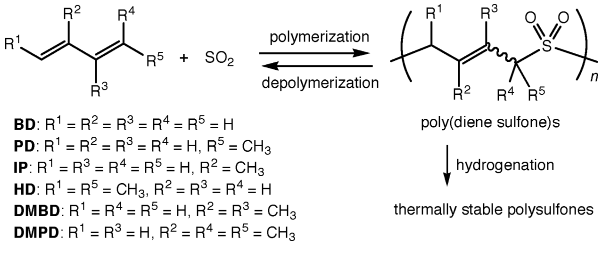
The free-radical copolymerization of alkyl-substituted 1,3-butadienes with sulfur dioxide using a redox initiating system in toluene at −78 °C produced poly(diene sulfone)s consisting of a highly alternating and 1,4-regiospecific repeating structure, irrespective of the position and number of alkyl substituents, and the highly regioselective propagation *via* a free radical reaction mechanism is well accounted for by DFT calculations using model reactions.

## Introduction

Radical chain polymerization has significant potential for controlled polymer syntheses with a well-designed chain structure, and the tacticity and sequence controls during a free radical polymerization process has been one of the challenging topics in the field of polymer synthesis.[1–5] Especially, the regiospecific polymerization of diene monomers is important because the physical properties of diene polymers significantly depend on the repeating structure of the diene monomer units, *i.e.*, the 1,2-, *cis*-1,4- and *trans*-1,4-structures.[6] The kinetics and thermodynamics of the cyclization of alkenyl radicals with high regioselectivity, which can occur in *exo* and *endo* fashions, have been intensively investigated.[7–10] On the other hand, only a few reports for regio-controlled diene polymerization by a radical reaction mechanism have been published, except for the inclusion polymerization of butadienes,[11–13] the topochemical polymerization of muconic and sorbic acid derivatives[14–16] and the alternating copolymerization of sorbic derivatives with molecular oxygen.[17,18] Poly(vinyl sulfone)s, often called poly(olefin sulfone)s, are synthesized by the radical copolymerization of olefins with sulfur dioxide ($SO_2$).[19,20] The main chain of the resulting poly(vinyl sulfone) is readily cleaved and therefore the poly(vinyl sulfone)s have been developed as resist materials.[21–26] In contrast, thermally-stable aromatic polysulfones are obtained by condensation polymerization, and they are used as engineering plastics for the mechanical and electrical parts of machines and automobiles, functional membranes for separation and fuel cells, and optical materials such as lens and films. Recent optoelectronics demand high performance polymers with an excellent thermal stability as well as optical and electrical properties. We reported the synthesis of poly(diene sulfone)s (PDSs) by the radical copolymerization of 1,3-butadiene (BD), isoprene (IP), and 2,4-hexadiene (HD) with $SO_2$ in a previous paper.[27] The resulting PDSs were converted into thermally stable polymers by hydrogenation of a C=C bond in the main chain. We also found that the PDSs have a highly controlled regiospecific repeating structure, *i.e.*, an exclusive 1,4-structure in the repeating unit of the alternating copolymers, despite a free radical polymerization mechanism. The regiospecificity is important for the synthesis of thermally stable PDS derivatives by hydrogenation, because the thermal stability of the polymers consisting of the 1,2-repeating units cannot be improved by hydrogenation of the polymers. In the present study, we synthesized the PDSs using alkyl-substituted 1,3-diene monomers, as shown in Scheme 1, and a mechanism for the regiospecific propagation is discussed based on the results of DFT calculations using model reactions. We also investigated the solubility and reactivity of the PDSs, which depended on the repeating structure.



Scheme 1

## Experimental section

### General procedures

The NMR spectra were recorded using a Bruker AV300N spectrometer with $CDCl_3$, dimethyl sulfoxide-$d_6$ (DMSO-$d_6$), and trifluoroacetic acid-$d_1$ (TFA-$d_1$) as solvents. The number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$), and polydispersity ($M_w/M_n$) were determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF) as the eluent

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*Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka, 558-8585, Japan. E-mail: matsumoto@a-chem.eng.osaka-cu.ac.jp; Fax: +81-6-6605-2981*

† This paper is dedicated to Prof. Athel Beckwith.

**Table 1** Conditions for the synthesis of PDS by the radical copolymerization of 1,3-butadienes with $SO_2$ and their properties[a]

| Monomer | Time (h) | Yield[b] (%) | $T_{95}$[c] (°C) | Solubility of PDS[d] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | TFA | DMSO | $CHCl_3$ | Acetone | THF |
| HD | 24 | 96.5[e] | 135(317) | soluble | soluble | soluble | soluble | soluble |
| PD | 12 | 99.9 | 141(322) | soluble | soluble | swelling | swelling | insoluble |
| IP | 12 | 92.9 | 156 | soluble | soluble | insoluble | insoluble | insoluble |
| DMPD | 24 | 13.2 | 130 | soluble | insoluble | insoluble | insoluble | insoluble |
| BD | 24 | 99.9 | 233(291) | insoluble | insoluble | insoluble | insoluble | insoluble |
| DMBD | 12 | 98.4 | 166 | insoluble | insoluble | insoluble | insoluble | insoluble |

[a] Copolymerization conditions: [1,3-diene] = 2.0 mol $L^{-1}$, [$SO_2$] = 5.0 mol $L^{-1}$, [*t*-BuOOH] = 20 mmol $L^{-1}$ in toluene. [b] Based on 1,3-diene monomers. [c] The $T_{95}$ is the 5% weight-loss temperature at the heating rate of 10 °C $min^{-1}$ in a nitrogen stream. The values in parentheses indicate those after hydrogenation. [d] TFA: trifluoroacetic acid, DMSO: dimethyl sulfoxide, THF: tetrahydrofuran, at room temperature. [e] $M_n = 1.1 \times 10^5$, $M_w/M_n = 2.0$, determined by SEC.

using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. The FT-IR spectra were recorded by a JASCO FT/IR 430 spectrometer using the KBr pellet method. The thermogravimetric and differential thermal analyses (TG/DTA) were carried out using a Seiko TG/DTA 6200 and a nitrogen stream at the heating rate of 10 °C $min^{-1}$. The decomposition temperature of the polymers was evaluated as the 5% weight-loss temperature ($T_{95}$) in the TG analysis. The differential scanning calorimetry (DSC) was carried out using a Seiko DSC-6200 at the heating and cooling rates of 10 °C $min^{-1}$. The wide-angle X-ray diffraction data were collected using a Rigaku RINT-Ultima 2100 X-ray diffractometer with Cu-K$\alpha$ radiation ($\lambda = 1.5418$ Å). All the DFT calculations were carried out using the Spartan'08 software package. A semi-empirical molecular orbital method was used for determination of the preferred conformations. The energies for the optimized structures were calculated at the B3LYP level of theory with the base functions of 6-311G(d,p), 6-311++G(3df,3pd) and cc-pVTZ. Several produced adduct radicals include an asymmetric carbon center, but the difference in the values of the diastereomers was small.

### Materials

The 1,3-diene monomers, BD, HD, 1,3-pentadiene (PD), 2,4-dimethyl-1,3-butadiene (DMBD), 2,4-dimethyl-1,3-pentadiene (DMPD) and 2,5-dimethyl-2,4-hexadiene (Tokyo Chemical Industry Co., Ltd. or Sigma-Aldrich Co., Ltd.), $SO_2$ (Sumitomo Seika Chemicals Co., Ltd.) and *tert*-butyl hydroperoxide (Sigma–Aldrich Co., Ltd.) were used as received without further purification. IP (Wako Pure Chemical Industries, Ltd.) and the solvents were distilled before use.

### Polymerization

A diene monomer (20 mmol) and *tert*-butyl hydroperoxide (0.04 mL, 0.2 mmol) in toluene (10 mL) were placed in a glass ampoule. The solution was degassed by the freeze-thaw technique. The cycle was repeated three times, then $SO_2$ (2.0 mL, 50 mmol) was added by vacuum distillation, and finally the ampoule was sealed. After polymerization for a given time at −78 °C, the polymerization mixture was poured into 200 mL of methanol. The polymer was filtered, washed with methanol, and then dried *in vacuo* at room temperature. The yield of the polymers was gravimetrically determined on the basis of the amount of charged diene monomers. Poly(HD-*alt*-$SO_2$), poly(PD-*alt*-$SO_2$) and poly(IP-*alt*-$SO_2$) were purified by repeated reprecipitation using chloroform or dimethyl sulfoxide as the solvent, and methanol as the precipitant.

## Results and discussion

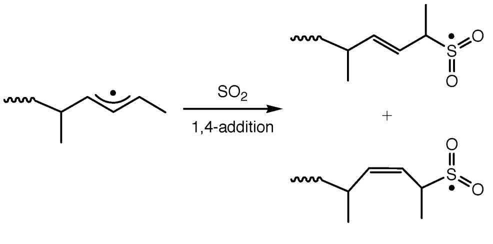
### Synthesis of PDS

The radical alternating copolymerization of various 1,3-diene monomers was carried out using an excess amount of $SO_2$ ([$SO_2$]/[diene] = 2.5 molar ratio) in toluene at −78 °C in the presence of *tert*-butyl hydroperoxide as the redox initiator in combination with $SO_2$. The results of the copolymerization are summarized in Table 1. The polymerizations quickly occurred even at a low temperature and the polymers were produced in a high yield. The PDSs were isolated as colorless solids in high yields, except for the sterically-hindered DMPD monomer. The 1,1-substituted ethylene (vinylidene type) structure is thermodynamically disadvantageous due to steric repulsion, resulting in a low yield of the poly(DMPD-*alt*-$SO_2$). Furthermore, we found that 2,5-dimethyl-2,4-hexadiene, *i.e.*, 1,1,4,4-tetramethyl-1,3-butadiene produced no polymer under similar polymerization conditions. A low ceiling temperature is reported for the various 1,1-disubstituted ethylene monomers, such as α-methylstyrene, isobutene, and α-substituted acrylates, and also for the copolymerization systems of the olefins and $SO_2$.[6] We found that an equilibrium monomer concentration ($[M]_e$) for HD decreases according to the temperature during the copolymerization with $SO_2$; $[M]_e = 1.4$ and 0.3 mol $L^{-1}$ at −30 and 20 °C, respectively, while a polymer was produced in a quantitative yield at −78 °C. More detailed thermodynamic studies of the polymerization of various diene monomers will be separately reported in the future.[28]

The poly(HD-*alt*-$SO_2$) was soluble in THF and the $M_n$ and $M_w/M_n$ values were determined by SEC; $M_n = 1.1 \times 10^5$ and $M_w/M_n = 2.0$. All the PDSs were readily decomposed upon heating. The $T_{95}$ values were 130–166 °C for the PDSs obtained in the present study, while poly(BD-*alt*-$SO_2$) showed the highest $T_{95}$ value (233 °C) because of reduced steric repulsion in the polymers. The $T_g$ value was determined to be 94.6 °C for poly(IP-*alt*-$SO_2$) and no $T_g$ was observed for the other PDSs below the onset temperatures of the decompositions based on the results of the DSC measurements.

## Characterization of PDS

The solubility of the PDSs was dependent on the polymer structure, *i.e.*, the position and number of alkyl substituents on the diene moiety of the used monomers. The solubilities of the PDSs are summarized in Table 1. Poly(HD-*alt*-$SO_2$) was soluble in TFA, DMSO, chloroform, acetone and THF, and insoluble in toluene, methanol, diethyl ether and *n*-hexane. Poly(IP-*alt*-$SO_2$) and poly(PD-*alt*-$SO_2$) were soluble in TFA and DMSO, but they were either insoluble or swelled in the other solvents. Poly(BD-*alt*-$SO_2$) and poly(DMBD-*alt*-$SO_2$) were insoluble in all the solvents. All the PDSs were amorphous based on the results of wide-angle X-ray diffractions. The repeating structure of the polymers was confirmed to consist of highly alternating and exclusively 1,4-repeating structures (Scheme 1), irrespective of the structure of the used monomers based on NMR and IR spectroscopies. The alternating copolymers were produced during the copolymerization of these diene monomers with $SO_2$, independent of the comonomer composition in the feed, because both monomers have no or much less reactivity for homopolymerization; *i.e.*, the monomer reactivity ratios, $r_1$ and $r_2$, are close to 0. The polymer configuration of the double bond in the main chain was random. This is due to no selectivity for the *cis-trans* configuration during the free-radical addition of an allyl radical (Scheme 2). A similar conclusion was reported in previous papers.[26,27] The solubility can be accounted for by the tacticity and the head-to-tail repeating structure of the resulting PDSs as follows. When a diene polymer including a 1,4 structure is produced, both the 1,4- and 4,1-additions should be differentiated as the propagation steps of the diene monomer. Three types of sequences, *i.e.*, head-to-tail, head-to-head and tail-to-tail, are produced during the radical polymerization of the dissymmetric monomers, such as IP, PD and DMPD (Fig. 1). Fig. 2 shows the $^{13}C$ NMR spectra of poly(IP-*alt*-$SO_2$), in which five split peaks were observed, representing each carbon. For the PDSs produced from HD and PD, isotactic (*meso*) and syndiotactic (racemo) repeating structures should also be considered. The poly(HD-*alt*-$SO_2$) implies two stereochemical centers per repeating unit. The peaks due to each carbon in the main chain are more split and broadened in these cases. Based on the NMR spectra for the other PDSs, it is concluded that all the PDSs are atactic. On the other hand, poly(BD-*alt*-$SO_2$) and poly(DMBD-*alt*-$SO_2$) have no asymmetric carbon center in the main chain. The solubilities of the PDSs are divided into several groups according to the repeating unit structures (Fig. 3): (i) PDSs insoluble in any solvent, consisting of a highly symmetric repeating structure, such as poly(BD-*alt*-$SO_2$) and poly(DMBD-*alt*-$SO_2$); (ii) PDSs soluble in TFA or DMSO and insoluble in the other solvents, including the head-to-tail structure, such as poly(IP-*alt*-$SO_2$) and poly(DMPD-*alt*-$SO_2$); (iii) PDSs soluble in several kinds of solvents, including the head-to-tail structure and a stereochemical center, such as poly(PD-*alt*-$SO_2$); and (iv) PDSs soluble in many solvents, including two stereochemical centers,



**Scheme 2**

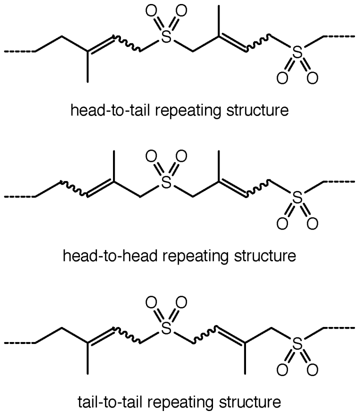


**Fig. 1** Head-to-tail, head-to-head, and tail-to-tail repeating structures included in poly(IP-*alt*-$SO_2$).

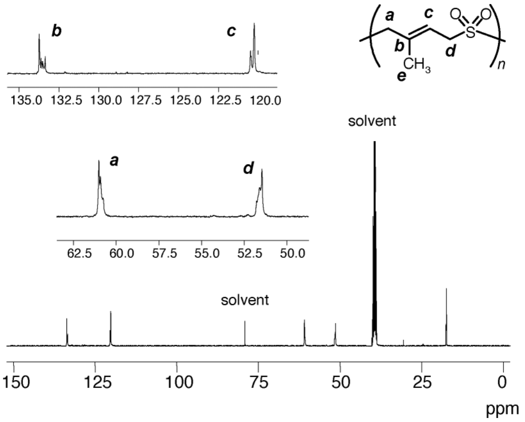


**Fig. 2** $^{13}C$ NMR spectrum of poly(IP-*alt*-$SO_2$).

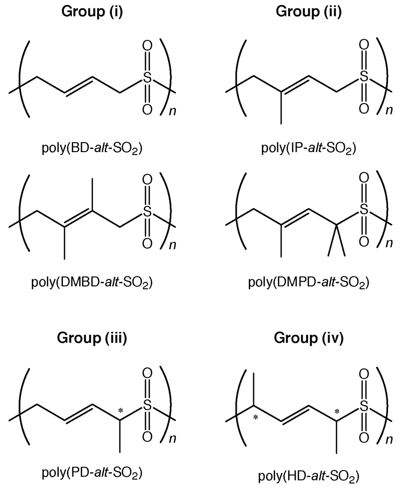


**Fig. 3** Classification of PDSs according to the type of repeating structures. Group (i): without a head-to-tail structure or an asymmetric center, Group (ii): with a head-to-tail structure, Group (iii): with a head-to-tail structure and an asymmetric center, and Group (iv): with asymmetric centers.

**Table 2** Results of the DFT calculations for the model radical copolymerization reactions of HD with $SO_2$

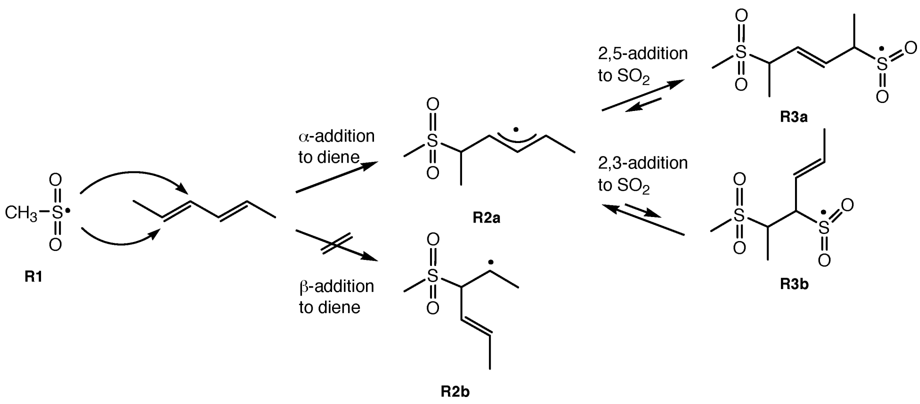
| | | | | $\Delta H$ (kcal $mol^{-1}$) | | |
|---|---|---|---|---|---|---|
| Radical | Monomer | Reaction | Product | 6-311G(d,p) | 6-311++G(3df,3pd) | cc-pVTZ |
| **R1** | HD | α-addition | **R2a** | −5.61 | −2.81 | −4.34 |
| | | β-addition | **R2b** | 17.6 | 20.1 | 19.2 |
| | | | | $\Delta(\Delta H)$ = −23.2 | −22.9 | −23.5 |
| **R2a** | $SO_2$ | 2,5-addition | **R3a** | −2.22 | −0.42 | 0.29 |
| | | 2,3-addition | **R3b** | 1.18 | 3.13 | 3.88 |
| | | | | $\Delta(\Delta H)$ = −3.4 | −3.6 | −3.6 |
| **R3a** | HD | α-addition | **R4a** | −4.52 | −1.69 | −3.51 |
| | | β-addition | **R4b** | 21.5 | 24.2 | 22.9 |
| | | | | $\Delta(\Delta H)$ = −26.0 | −25.9 | −26.4 |
| **R3b** | HD | α-addition | **R4c** | −1.00 | 1.76 | 0.41 |
| | | β-addition | **R4d** | 25.3 | 27.6 | 26.6 |
| | | | | $\Delta(\Delta H)$ = −26.3 | −25.8 | −26.2 |
| **R4a** | $SO_2$ | 2,5-addition | **R5a** | −4.95 | −1.72 | −1.38 |
| | | 2,3-addition | **R5b** | 2.77 | 4.62 | 5.28 |
| | | | | $\Delta(\Delta H)$ = −7.7 | −6.3 | −6.7 |
| **R4c** | $SO_2$ | 2,5-addition | **R5c** | −6.56 | −3.86 | −3.99 |
| | | 2,3-addition | **R5d** | 4.13 | 6.76 | 7.32 |
| | | | | $\Delta(\Delta H)$ = −10.7 | −10.6 | −11.3 |

such as poly(HD-*alt*-$SO_2$). The solubility increased in the order of the groups (i) to (iv).

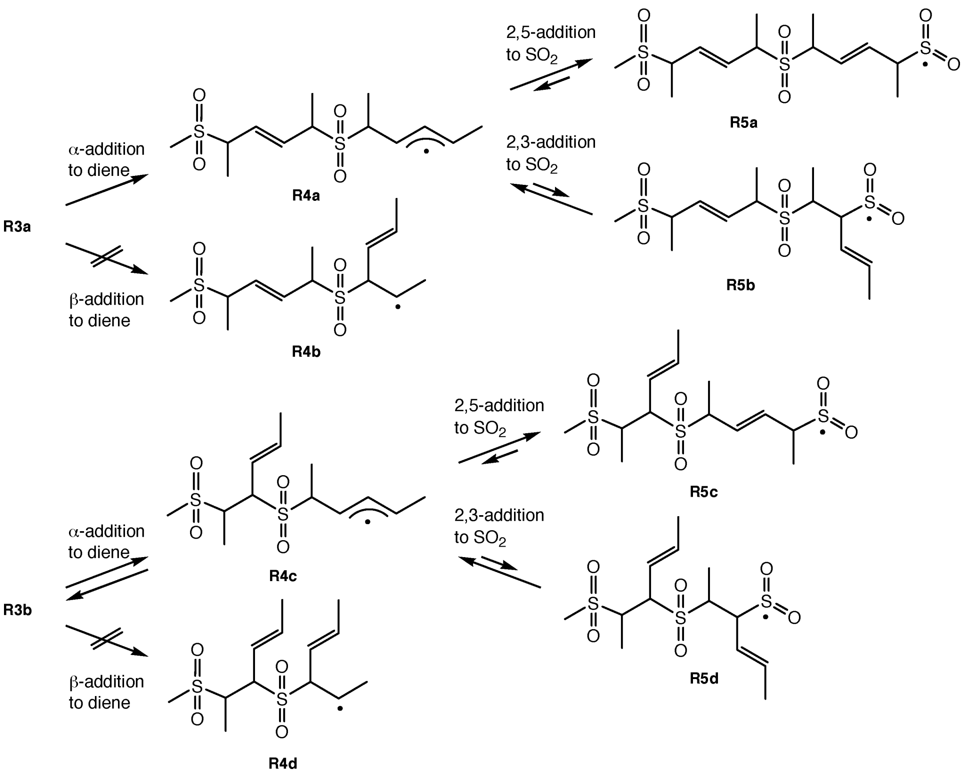
## DFT calculations for regiospecific propagation

In order to elucidate the highly regiospecific reaction *via* a free radical propagation mechanism, DFT calculations were carried out using the model reactions, as shown in Schemes 3 and 4. It had been pointed out that the kinetic control of the regio- and stereoselectivities is difficult during the free radical reactions of acyclic compounds, such as the intermolecular radical addition to a C=C double bond until the sophisticated and relevant approach shown in the 1990s.[29] An early, reactant-like transition state, which is often observed for radical reactions under kinetic control, is advantageous for the prediction of a transition-state model and the avoidance of steric hindrance during the reaction, but is also accompanied by poor selectivity in some cases.[30] On the other hand, it has been well known that the thermochemical approach is useful for estimating the relative rates and directions of the addition of a radical to a C=C bond, although the stereoelectronic effects also play an important role in determining the regiochemistry of many addition reactions.[31] The thermodynamic analysis is also useful for estimating the propagating fashion during the radical alternating copolymerization of a diene monomer with $SO_2$, in which the contribution of the depropagation is important due to the low ceiling temperatures. Therefore, we evaluated a change in the heat of formation for the reaction of a propagating radical into a monomer (diene or $SO_2$) using three different levels of basis sets for the calculations. The transition states were not discussed in this study. The results are summarized in Table 2.

The sulfonyl radical, **R1** favors a reaction at the α-position of the diene (*i.e.*, 2-position of HD) due to the formation of an allyl radical during the reaction of a sulfonyl radical to a diene monomer (Scheme 3). The value of the enthalpy change for the addition at the α-position was negative and the difference in the enthalpy changes for the additions at the α- and β-positions [$\Delta(\Delta H)$] was −23 kcal $mol^{-1}$, independent of the level of the basis sets used for the calculation. During the addition of **R2a** to $SO_2$, both the 2,5- and 2,3-propagations of the allyl radical should be considered. Each propagation reaction produces the sulfonyl radicals, **R3a** and **R3b**, respectively. The $\Delta H$ value for the former reaction is negative and seems to be favored, while the latter is positive. However, the difference in these values is quite small



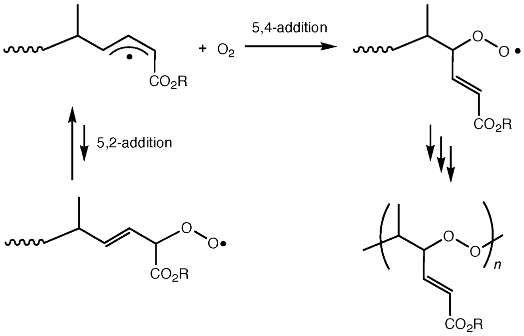
Scheme 3



Scheme 4

(3.4 kcal mol$^{-1}$). This suggests that both the reaction pathways have a chance to occur during the copolymerization.

The larger radicals, **R3a** and **R3b** also selectively favor the addition to the α-position of the diene; $\Delta(\Delta H) = -26$ kcal mol$^{-1}$ (Scheme 4). This result is similar to the addition tendency of the smaller radical **R1**. The selectivity during the propagation of the larger allyl radicals also provided a result similar to that for the smaller radical **R2a**. The high regioselectivity of the 2,5-propagation of the allyl radicals cannot be accounted for by the relatively small $\Delta(\Delta H)$ values (6–10 kcal mol$^{-1}$). During the propagation step of the copolymerization of $SO_2$ with olefins and dienes, the depropagation effect is not negligible because of a low ceiling temperature, as already described. Especially, the addition step of the allyl radical to $SO_2$ is slow and the reverse reaction should be considered. The sulfonyl radical produced *via* the 2,3-propagation, *e.g.*, **R3b**, **R5b** and **R5d**, can readily undergo depropagation, judging from the positive $\Delta H$ values and the significant steric hindrance of the repeating units. We previously reported the 1,2-regioselective polymerization of 1,3-diene monomers during the radical alternating copolymerization with molecular oxygen (Scheme 5).[32,33] The selectivity was accounted for by theoretical calculations using model reactions consisting of two steps, involving the addition of a methyl peroxy radical to a 1,3-diene monomer and the reaction of the resulting allyl radical with oxygen. The first step was mainly controlled by the difference in the heat of formation of the intermediate radicals, and the second step was determined by the bond dissociation energy of the newly formed C–O bond, which is reversibly cleaved.[34] The reversible propagation steps are key for controlling the regioselectivity during the alternating copolymerizations of diene monomers with $SO_2$ and oxygen. Thus, the high regioselectivity observed for the propagation of the diene monomers during the alternating radical copolymerization in this study is also accounted for by the contribution of the reverse (depropagation) reactions.



Scheme 5

## Hydrogenation of PDS

The hydrogenation of the PDSs provides thermally stable polysulfones. The hydrogenation is effectively carried out at a relatively low temperature below 100 °C because the PDSs are readily degraded before the hydrogenation. A drastic increase in the onset temperature of decomposition was observed after the hydrogenation, as shown in Table 1. The $T_{95}$ values were 135 and 141 °C and they increased to 317 and 322 °C, respectively, after the quantitative hydrogenation for poly(HD-*alt*-$SO_2$) and poly(PD-*alt*-$SO_2$). An increase in the thermal stability of the PDSs by the hydrogenation is evidence for the 1,4-regioselective propagation of the diene monomers during the copolymerization, because an increase in the thermal stability is expected for only the hydrogenation of the 1,4-polymers, and not for the 1,2-polymers. For poly(IP-*alt*-$SO_2$), poly(DMPD-*alt*-$SO_2$) and poly(DMBD-*alt*-$SO_2$), the hydrogenation conversion was much lower, because of the steric hindrance of the methyl substituents on the double bond of the polymers. The physical properties of the thermally stable polysulfones prepared by the hydrogenation of the PDSs are now under investigation. The detailed polymerization reactivity as well as the polymer characterization of the various diene monomers will be separately reported in the near future.[28]

## Conclusions

During the free-radical copolymerization of alkyl-substituted 1,3-butadienes with $SO_2$ using a redox initiating system in toluene at −78 °C, the PDSs consisting of a highly alternating and 1,4-regiospecific repeating structure are produced, irrespective of the position and number of the alkyl substituents. We investigated the effect of the alkyl substituent of the butadiene moiety on the polymerization reactivity as well as polymer properties, such as the solubility and thermal stability. The addition of a sulfonyl radical to the $\alpha$-position of a diene monomer and the 1,4-propagation of an allyl radical is well accounted for by the DFT calculations using model reactions. The calculations revealed some reversible propagation steps and highly regiospecific sequences despite a free radical propagation mechanism. The solubility and hydrogenation reactivity of the PDSs sensitively depended on the repeating unit structures, *i.e.*, the position and number of the alkyl substituents. The regiocontrolled repeating structure is important for the production of thermally stable polymers after the polymer hydrogenation. The hydrogenated PDSs are expected to be applied as new types of transparent heat-resistant polymers.

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